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The project entitled "Adsorption of Hazardous Compounds to Mineral Surfaces" involved five faculty members from the University of Wyoming's Departments of Chemistry, Geology, Soil Science, and Mathematics. The contribution from each individual research is enclosed in this final report. The results include two methods of modifying clays with cationic surfactants to enhance the adsorption of organic contaminants; modification of clays with cyclodextrins; studies of small acid adsorption to minerals; FTIR studies of adsorption to silicates; and stochastic analysis of flows in soils. The work with modified clays has lead to quantitative relationships that can be used to predict the sorptive behavior of yet untested modifiers. This data can be used to design improved treatment walls. Both Canon and Vance worked on a variety of contaminants to demonstrate these relationships. We synthesized a new surfactant that contains chlorines and showed enhanced sorption of chlorinated ethylenes. Buttry and Drever showed that small acids such as oxalic are capable of adsorbing to silica and can chelate with the mineral surface. The strong chelation is believed to lead to weathering or dissolution of the mineral surface. Buifry also showed that FTIR can be used to follow adsorption kinetics and to study surfactants adsorbed to mineral surfaces.					
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Soil and Environmental Chemistry Group

Adsorption of Hazardous Organic Compounds by Mineral Surfaces

The following are summaries of various projects completed for the Air Force project:

1. Intercalation of Carboxymethyl- β -Cyclodextrin into Magnesium-aluminum Layered Double Hydroxide (published in J. Chem. Soc. Dalton Trans.)

New intercalated compounds have been prepared by incorporating carboxymethyl- β -cyclodextrin (CMCD) into magnesium aluminum layered double hydroxide (Mg/Al LDH). The sorptive uptake of CMCD(3) and CMCD(14), with a degree of carboxymethyl substitution of 3 and 14, respectively, by Mg/Al LDH was examined at 65°C, and the resulting complexes were characterized using XRD and FT-IR. Results indicated that Mg/Al LDH could uptake approximately twice as much CMCD(3) as compared to CMCD(14). Results of XRD and FT-IR confirmed that both CMCD(14) and CMCD(3) could be intercalated into Mg/Al LDH interlayers due to an ion exchange process. After exposure to CMCD(14) and CMCD(3), the d-spacing of Mg/Al LDH expanded from 8.74 Å to 15.48 Å and 20.63 Å, respectively. Intercalated CMCD(14) molecules formed monolayer coverage in the Mg/Al LDH interlayers, with the cavity axis perpendicular to the LDH layer, while CMCD(3) molecules adopted either a parallel monolayered arrangement or a perpendicular bilayer-like coverage. Both CMCD(14) and CMCD(3) molecules were believed to be loosely packed within the Mg/Al LDH interlayers.

2. Molecular Inclusion Characteristics of Hydrophobic Organic Compounds by a Modified B-cyclodextrin Incalated Within a Layered Double Hydroxide (Revised and resubmitted, should be accepted by J. Incl. Phenom. Mol. Recog. Chem.)

A study was conducted to evaluate the inclusion properties of various nonionic hydrophobic organic compounds by a novel intercalate derived from magnesium-aluminum layered double hydroxide (Mg/Al LDH) and carboxymethyl- β -cyclodextrin with a degree of substitution of 3 [CMCD(3)]. The isotherm sorption results at 25°C showed that the CMCD(3)-Mg/Al LDH intercalate could retain all the organic compounds studied and its sorption affinity for organic compounds was positively related to their hydrophobicities. The host-guest interaction was attributed to a partition process of the organic compounds into the cyclodextrin cavity, while a stereoselective interaction might also be involved due to the intercalation of CMCD(3) within Mg/Al LDH interlayers.

3. Selectivity and Molecular Sieving Effects of Organic Compounds on the Intercalate of B-cyclodextrin and Layered Double Hydroxide (Submitted to Clays and Clay Minerals)

This study dealt with the sorption characteristics of 10 nonionic hydrophobic organic compounds by a novel intercalate derived from magnesium-aluminum layered double hydroxide (Mg/Al LDH) and carboxymethyl- β -cyclodextrin with a degree of substitution of 14 [CMCD(14)]. The isotherm sorption results at 25 °C showed that the CMCD(14)-Mg/Al LDH intercalate exhibited size/shape selectivity for the organic compounds studied. This selectivity appeared to result from the intermolecular micropores and the hindered accessibility of the cyclodextrin cavity. Such selectivity and sieving effect may be useful in chromatographic applications as well as in selective removal of organic pollutants from water.

4. BTEX Sorption by Organo-Clays: Cosorptive Enhancement and Equivalence of Interlayer Complexes (Published in Soil Sci. Soc Am. J.)

Aqueous organic contaminants are effectively sorbed by organo-clays. Organo-clays were prepared from montmorillonite (SWy-1, SAz-1) and vermiculite (VSC) clay minerals by exchanging quaternary, alkylammonium cations for the inorganic exchange cations; thus, a variety of clay-charge/organic-cation combinations were formed. Dodecyl-trimethylammonium (DTMA), hexadecyltrimethylammonium (HDTMA), didodecyl-dimethylammonium (DDDMA), and dioctadecyldimethylammonium (DODMA) organic cations were used. An aqueous mixture of BTEX (benzene, toluene, ethylbenzene, xylenes) consistent with unleaded gasoline was used to relate organo-clay sorptivity to structure. Greater sorption of the BTEX mixture constituents than the pure compounds occurred when total sorbed BTEX loadings on the organo-clays exceeded 10 g/kg. A co-sorption effect caused curvilinear isotherms and enhanced BTEX mixture sorption; BTEX sorption increased the organo-clay organic-matter content which promoted additional BTEX sorption.

The sorptivities of the organo-clays were generally proportional to the organic carbon contents; although SAz-DDDMA and VSC-HDTMA, with 20 to 30% less carbon, had twice the BTEX sorptivity of SAz-DODMA and VSC-DDDMA. No relationship was found between surface area and BTEX sorption. A straight-chain alkyl cation conferred 5 times greater BTEX sorption to an organo-clay than did a comparable cyclic alkyl cation. This suggests that rearrangements in the alkyl groups may facilitate sorption in a manner analogous to solvation. Organo-clay BTEX sorptivity was also governed by the type of alkylammonium complex; a paraffin complex with a 25.4 to 27.6 Å basal spacing was optimal. Organo-clays of similar basal spacing prepared using different clays and alkylammonium cations had equivalent sorptive phases. Selection of an appropriate combination of clay and organic cation can optimize contaminant sorption by organo-clays.

5. Sorption of the Ionizable Organic Compound, Dicamba, (3,6-Dichloro-O-Anisic Acid) by Organo-Clays (Published in Chemosphere)

The sorption/desorption of 3,6-dichloro-o-anisic acid (dicamba) by hexadecyl-trimethylammonium (HDTMA)- and dioctadecyldimethylammonium (DODMA)-exchanged smectites was studied at different concentrations and pH levels to evaluate the capability of organo-clays to sorb an ionizable hydrophobic compound. Dicamba-organo-clay complexes were also prepared and characterized by x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) to determine the possible sorption mechanisms involved. The results indicated that dicamba, although water-soluble, ionizable, and potentially mobile, was strongly sorbed by the organo-clays and was not readily desorbed. Sorption isotherms could be divided into two distinct regions; a non-linear region at low dicamba concentrations and a linear region at high dicamba concentrations; partitioning was believed to be the dominant process involved in the sorption of dicamba at higher concentrations.

Organo-clays with higher organic carbon contents (i.e., amount and molecular weight of exchanged organic cation (HDTMA or DODMA)) usually resulted in greater dicamba sorption. Solution pH significantly affected the sorption of dicamba by organo-clays, with the isotherm inflection point near the dicamba pK_a value. Nearly twice as much dicamba could be sorbed in the molecular form as compared to its anionic, deprotonated form. Excessive DODMA was found to increase dicamba sorption at pH levels greater than the dicamba pK_a , which was possibly caused by charge reversal of the organo-clay surface. Possible sorption mechanisms, based on XRD and FT-IR data, suggest hydrophobic and ionic attractions both contributed to the sorption of dicamba.

6. Sorption of Trichloroethylene by Organo-clays in the Presence of Background Humic Substances (Submitted to Water Research)

A study examined trichloroethylene sorption characteristics by organo-clays (hexadecyltrimethylammonium (HDTMA) and didodecyldimethylammonium (DDDMA) exchanged smectites (SWy-1 and SAz-1)) in aqueous solutions both in the presence and absence of humic substances (aldrich humic acid and peat fulvic acid), as well as the impacts of the preloading of humic substances. The results indicated uptake of humic substances by organo-clays and the effects of humic substances on trichloroethylene sorption by organo-clays was dependent on the type of organo-clay and humic substance. Selection of an appropriate combination of clay and organic cation can optimize the removal of trichloroethylene as well as humic substances from aqueous solutions by organo-clays. Organo-clays may be an alternative to activated carbon sorbents in specific water treatment processes.

7. Removal of Polynuclear Aromatic Hydrocarbons by Organo-clays from Water/methanol Mixtures (In preparation for Environ Sci. and Technol.)

A study was conducted to evaluate the effectiveness of 10 organo-clays for removal of PAHs (pyrene and anthracene) in the presence of methanol. Preliminary results indicated that cosolvent theory could be successfully used to predict the sorption behaviors of PAHs by organo-clays from water/methanol mixtures, and that organo-clays had strong affinities for both pyrene and anthracene. However, the sorption affinities varied among the organo-clays, depending on the combination of clay and organic cation. This study has implications on understanding the usefulness of organo-clays as sorbents for PAHs pollutants in real-world, complex waste streams such as industrial wastes and landfill leachates which are usually composed of a mixture of water, pollutants, and miscible organic solvents.

8. *Modeling BTEX Sorption by Organo-Clay Derivatives* (In preparation for Soil Sci. Soc Am. J.)

The objectives of the present study were to quantify BTEX (benzene, toluene, ethylbenzene, o-, m-, p- xylene) sorption by various organo-clay derivatives using different isotherm models and to evaluate competitive sorption characteristics of these hydrocarbons in relation to organic-cation mass and organo-clay basal spacing. Two montmorillonite-derivatives including trimethylphenylammonium (WNM-C₉H₁₄N⁺) and trimethylammonium adamantane (WNM-C₁₃H₂₄N⁺), and three hectorite-derivatives including trimethylphenylammonium (CNH-C₉H₁₄N⁺), trimethyl-ammonium biphenyl (CNH-C₁₅H₁₈N⁺) and trimethylammonium fluorene (CNH-C₁₆H₁₈N⁺) were used in this study. The organo-clays were prepared by exchanging the inorganic cations in the clay minerals with the quaternary alkyl ammonium cations. A batch sorption study was conducted with a BTEX mixture that contained the constituent compounds in proportions consistent with the composition of unleaded gasoline.

The results for all of the six compounds indicated that, the concentrations in sorbed phase increased curvilinearly with that in solution phase. Corresponding to the equilibrium concentrations the amounts of sorbed hydrocarbons were higher for C₉H₁₄N⁺ derivatives as compared to C₁₃H₂₄N⁺ derivative followed by C₁₅H₁₈N⁺ and C₁₆H₁₈N⁺ derivatives. Solid phase partitioning of ethylbenzene, o-xylene and m-xylene was maximum in CNH-C₉H₁₄N⁺, and that of benzene was greatest in WNM-C₉H₁₄N⁺. Hydrocarbon sorption data were statistically ($p < 0.1$) fitted to Langmuir, Freundlich and Temkin models. The Langmuir model was fitted to BTEX sorption on WNM-C₉H₁₄N⁺, WNM-C₁₃H₂₄N⁺ and CNH-C₉H₁₄N⁺ whereas adsorption of CNH-C₁₅H₁₈N⁺ and CNH-C₁₆H₁₈N⁺ did not conform to this model. The site-densities of WNM-C₉H₁₄N⁺, WNM-C₁₃H₂₄N⁺ and CNH-C₉H₁₄N⁺ for BTEX were estimated to be $1.89\text{-}11.4 \times 10^{17}/\text{m}^2$, $2.80\text{-}19.1 \times 10^{17}/\text{m}^2$, and $1.60\text{-}44.2 \times 10^{17}/\text{m}^2$, respectively, indicating a high order (10^{17}) of magnitude for all three organo-clays. Relatively higher values of the adsorbate buffering capacity (K_1B_1) of the C₉H₁₄N⁺ derivatives than WNM-C₁₃H₂₄N⁺ suggested that sorption on

$C_9H_{14}N^+$ -clays would be more effective. The K_tB_1 further indicated that the values for the montmorillonite derivative were either comparable to or higher than the hectorite derivative for the same cation $C_9H_{14}N^+$. The binding affinity (K_f) values obtained from the Freundlich model was consistently higher for $C_9H_{14}N^+$ derivatives as compared to the WNM- $C_{13}H_{24}N^+$. However, the maximum K_f values were noted for CNH- $C_{15}H_{18}N^+$ and followed by CNH- $C_{16}H_{18}N^+$. The ranges of n_f values for benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene were 0.90-1.75, 0.78-1.74, 0.64-1.88, 0.61-1.62, 0.65-1.67, and 0.63-1.88, respectively. The lowest n_f values for all six hydrocarbons were consistently observed for CNH- $C_{15}H_{18}N^+$, and the highest values were mostly found in case of $C_9H_{14}N^+$ -clays. The Temkin constant K_{t1} , pertaining to heat of chemisorption, was found to decrease linearly with molecular weight of the cations present in the organo-clay derivatives thereby suggesting the organo-clays with low molecular weight cations would have greater heat of chemisorption, which physically means greater hydrocarbon retention.

The slope of a differential change in K_{t1} with cationic molecular weight followed the order of toluene > m-xylene > p-xylene > o-xylene > ethylbenzene > benzene. Greater K_{om} values indicated greater partitioning of the hydrocarbons into the organo-clays; thus, maximum partitioning of all six hydrocarbons will be caused by WNM- $C_9H_{14}N^+$ organo-clay followed by CNH- $C_9H_{14}N^+$ and WNM- $C_{13}H_{24}N^+$ derivatives; CNH- $C_{15}H_{18}N^+$ and CNH- $C_{16}H_{18}N^+$ organo-clays corresponded to much lower K_{om} values; a similar sequence in the magnitude of ΔG (sorption free energy) also supported this finding. The positive (+) values of $\log K_{om}/K_{ow}$ ratio indicated that WNM- $C_9H_{14}N^+$, WNM- $C_{13}H_{24}N^+$ and CNH- $C_9H_{14}N^+$ derivatives could result in greater partitioning of BTEX as compared to octanol medium. Preferential partitioning of benzene and toluene was also indicated by the greater magnitude of $\log K_{om}/K_{ow}$, which was due to greater solubility of these two hydrocarbons as compared to ethylbenzene and the xylenes. This was further reflected in the plot showing the effect of organic-cation thickness on BTEX partitioning. Corresponding to the d_{001} values, $\log K_{om}/K_{ow}$ for benzene and toluene were higher than other hydrocarbons. The $\log K_{om}/K_{ow}$ values for all six hydrocarbons decreased following the same pattern as the basal spacing increased. This means greater partitioning of the hydrocarbons will occur with organo-clays with lower interlayer spacing, for example $C_9H_{14}N^+$ derivatives. Knowledge obtained from this study is expected to contribute to the understanding of future contaminant remediation techniques.

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FINAL REPORT ON ACTIVITIES UNDER AFOSR CONTRACT

J.I. Drever, L.L. Stillings, S.R. Poulson

Our research was focused on the adsorption of organic anions on the surfaces of the common silicates that make up the bulk of natural aquifers (feldspars and quartz). Carboxylic acids and their anions adsorb strongly to many common silicates and the adsorbed polar organic compound may serve as a substrate for adsorption of non-polar species. Associated with the adsorption phenomenon, organic anions accelerate the dissolution of these silicates, so the presence of such organic compounds may affect the physical and chemical properties of the aquifer.

Most of our work was conducted using oxalate as a model compound. We showed that, despite reports to the contrary in the literature, oxalate does not adsorb on quartz surfaces and does not accelerate the dissolution rate of quartz. On the other hand, oxalate does adsorb onto feldspar surface by coordinating at surface aluminum sites, and this adsorption may cause an increase in the dissolution rate of the mineral. The magnitude of the effect depends on the composition of the feldspar and the pH of the solution.

We also provided analytical facilities to other investigators in the group, particularly X-ray diffraction analyses for George Vance and his colleagues.

Publications wholly or partially supported by the contract

- Poulson, S.R., Drever, J.I., and Stillings, L.L. (1996) An experimental study of aqueous Si-oxalate complexing and oxalate adsorption onto quartz. Fourth International Symposium on the Geochemistry of the Earth's Surface (ed. S.H. Bottrell) International Association of Geochemistry and Cosmochemistry, p. 624-627.
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- Drever, J.I. and Stillings, L.L. (1997) The role of organic acids in mineral weathering. Colloids and Surfaces, v. 120, p. 167-182.
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Abstracts

- Stillings, L.L., Brantley, S.L., and Drever, J.I. (1995) Does oxalic acid increase dissolution rates for feldspar minerals? Amer. Chemical Society National Meetings, Anaheim, CA, Book of Abstracts, GEOC, 055.
- Drever, J.I. and Stillings, L.L. (1995) The role of organic acids in mineral weathering. Invited plenary lecture, International Humic Substances Society Conference "Humic Substances in the Environment", Atlanta, GA, Abstracts, p. 16-17.
- Stillings, L.L., Angevine, C.L., Drever, J.I., and Machesky, M.L. (1997) Single- and multi-site models of protonation at porous feldspar surfaces. Book of Abstracts, American Chemical Society National Meetings, GEOC 122.
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AFOSR Final Report - Daniel A. Buttry - October 7, 1997

The primary focus of our component of the effort has been the development of *in situ* spectroscopic methods to study the adsorption and desorption of various contaminant model compounds at mineral surfaces. Toward this end, we have developed a new methodology for using ATR-FTIR (attenuated total reflection-Fourier transform infrared) spectroscopy to probe adsorption of various organic compounds at mineral surfaces. In this method, a flow cell is constructed so that it can be placed against an ATR optical element (such as a ZnSe crystal) in such a way as to trap the mineral particles within close proximity to the surface of the ATR element. Due to the evanescent optical field that exists just outside of the ATR element, the infrared spectrum of the portion of the particles that are within the evanescent region can be sampled, as well as the spectra of any adsorbed species that are present. In this way, one obtains the vibrational spectrum of the adsorbate species.

There are several intrinsic advantages to this technique. The most significant one is that the strong interactions that lead to adsorption of most adsorbates will produce significant changes in the vibrational spectrum of the adsorbate, allowing it to be distinguished spectrally from the corresponding species in solution. Thus, this method will typically provide the capability to differentiate easily between solution phase species and adsorbed species.

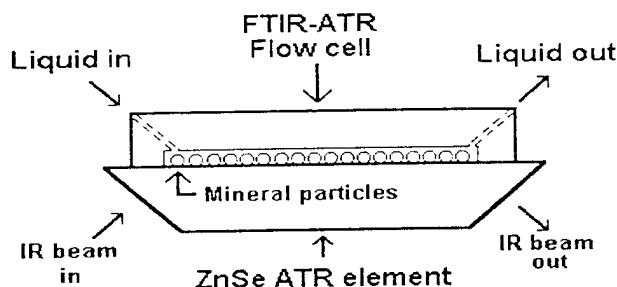


Figure 1 – Schematic of the ATR-FTIR flow cell used to study adsorption at the surfaces of mineral particles.

This method has been applied to several different systems. Our initial experiments employed silica particles as the adsorbent phase. In one set of experiments, we examined the adsorption of species bearing carboxylate functionalities (e.g. acetate) at silica surfaces. As can be seen below in Figure 2, we found that the adsorption of such species does not occur spontaneously. This is because over the pH range that we studied (4-8), the surface charge of silica is neutral to slightly negative, leading to electrostatic repulsion of the negatively charged acetate. Further, the silica surface is not expected to provide sufficiently electrophilic adsorption sites for acetate (i.e. there are no attractive sites at which acetate could adsorb via complex formation). However, when metal ions, such as Ca^{2+} , are present in solution which can enter into complexes with the surface siloxane groups, the carboxylate species adsorb onto the surface. This adsorption is presumably due to complexation between the adsorbed metal ions and the carboxylates functionalities. A manuscript on this study is in preparation.

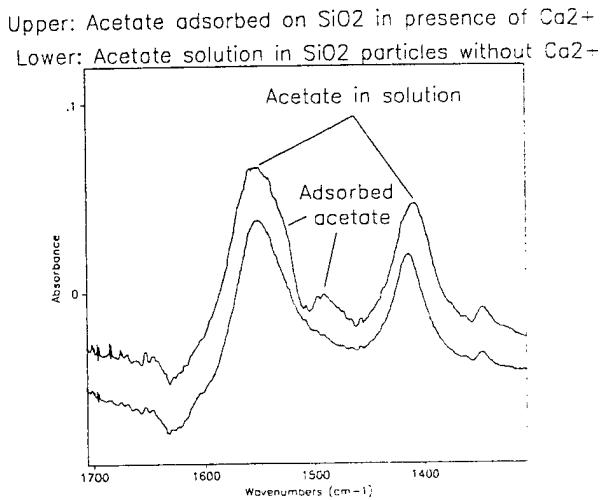


Figure 2 - Spectra of acetate (Ac) anion in the pore volume of SiO₂ particles. Upper: 0.1 M NaAc + 10 mM CaCl₂. Lower: 0.1 M NaAc without CaCl₂. Obtained in ATR mode with ZnSe element on a Bomem MB 100 FTIR.

The lower curve in the Figure 2 shows the spectrum of acetate anion in aqueous solution (peaks at 1560 cm⁻¹ from the antisymmetric carboxylate stretch and 1415 cm⁻¹ from the symmetric carboxylate stretch). These bands are observed because of the portion of the acetate solution that is trapped within the pore volume of the SiO₂ particles adjacent to the ZnSe ATR element. The upper curve shows the spectrum that is obtained when the SiO₂ particles are exposed simultaneously to acetate and Ca²⁺ ion. This spectrum clearly shows the responses from both the solution-phase acetate **and** the adsorbed acetate, as indicated in the figure. The peaks from the adsorbed acetate (shoulder at 1540 cm⁻¹ and peak at 1495 cm⁻¹) are shifted from those of the solution-phase species in a manner that is consistent with bidentate interaction with the adsorbed Ca²⁺ (i.e. both acetate oxygens are attached to the adsorbed acetate).

These data were important because they validated the essential assumptions behind the choice of the ATR-FTIR technique, namely that it would be possible to spectrally differentiate the solution phase and adsorbed species by virtue of changes in their vibrational spectra. A manuscript on this study is in preparation.

The attached manuscript (submitted to *Langmuir*) describes a study of the adsorption of the surfactant dodecyltrimethylammonium (DTAB) cation at silica surfaces. These systems are of importance to the USAF because they have the potential to be used in remediation of subsurface contaminants, such as TCE. Figure 3 below shows the isotherm obtained for adsorption of DTAB at the silica surface, along with isotherms calculated for various

adsorption models. These data demonstrate convincingly that it is also possible to observe adsorbed species even when their vibrational spectra are *not* substantially different from those of the solution phase species.

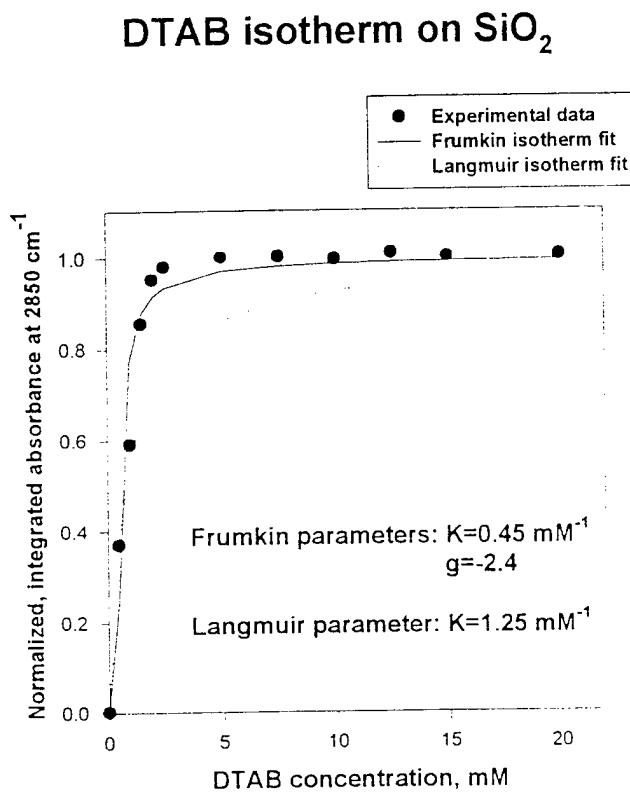


Figure 3 – Adsorption isotherm for DTAB at silica, with calculated model isotherms, demonstrating Frumkin-like adsorption behavior.

We have achieved several long term goals that derive from this general area of interest. First, we have developed a method that can be used to identify the nature of the interactions between the contaminants and the mineral surfaces. Our objective in this regard was to develop an ability to predict the extent of adsorption of a given contaminant on a given mineral, where the prediction will be based solely on the molecular structure of the contaminant and the nature of the mineral surface. Second, we developed the experimental methodology that will allow us to measure the desorption rates of contaminants from mineral surfaces. The objective of this component of the work was to provide a set of kinetic data on desorption rates that will be of use to that part of the scientific community involved in modeling the subsurface transport of contaminants. The reasoning behind this effort is to gain a better understanding of dispersive effects in subsurface transport. Third, we investigated the adsorption of amphiphilic and hydrophobic compounds. The objective here was to learn how the adsorption of surfactants influences the adsorption and desorption of hydrophobic contaminants.

An *In-situ* ATR-FTIR Study of DTAB Adsorption at a Silica Gel Surface

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Introduction

The adsorption of surfactants from solution at the solid-liquid interface is of great importance both because of theoretical interest in such processes and because of the many applications in which they are important. As a consequence of this high level of interest, there are many recent studies of the phenomenon.¹⁻³ Applications in which surfactant adsorption is important include detergency, ore floatation, microelectronics and environmental remediation. A particularly interesting area has to do with the use of surfactants in environmental remediation.^{4,5} There are at least two distinct modes of operation in such efforts. In one, the micellar phase of the surfactant is used to mobilize hydrophobic subsurface contaminants, so that they may be removed more effectively using pump-and-treat methods. In this application, surfactant adsorption is not desirable, because it reduces the amount of surfactant that is available to form micelles. In another mode of operation, the surfactant is used to temporarily immobilize a hydrophobic subsurface contaminant by trapping it within the hydrophobic layers created by surfactant adsorption at mineral surfaces. In this case, adsorption of the surfactant is critical to the success of the temporary immobilization. Thus, information about the adsorption of surfactants at mineral surfaces is essential for the proper engineering of such remediation efforts. Due to the usually negatively charged nature of sediments and soil particles, cationic surfactants such as DTAB can adsorb strongly onto these particles. However, little is known about the details of such adsorption at the microscopic level. This study describes the use of *in-situ* ATR-FTIR methods to monitor the adsorption of DTAB at the aqueous solution/silica interface.

The use of *in-situ* FTIR to study the solid/liquid interface has a history that can be traced back to the early 1970's. Rochester and co-workers^{6,7} studied adsorption of organic molecules from carbon tetrachloride solutions onto silica. Tejedor-Tejedor and co-workers⁸⁻¹⁰ applied the cylindrical internal reflection (CIR-FTIR) method to the study of adsorption at the mineral oxide/water interface. By utilizing the attenuated total reflection (ATR) method, some mineral/water interface have been studied, such as the silica/water interface¹¹, goethite/water interface^{8,9}, alumina/water interface^{1,12}, etc. These studies showed that ATR is capable of semi-quantitative characterization of adsorption behavior at aqueous interfaces. A principal advantage of this method over other methods is that the limited penetration depth of the beam into the solution reduces the absorption of the beam by water, which is the usual problem with infrared experiments in aqueous solutions. Comparison to *ex-situ* FTIR methods used in surfaces studies^{13,14} shows that another advantage of the *in-situ* ATR-FTIR

method is that it has the possibility to be used to monitor the kinetics of the adsorption and/or desorption processes.

Experimental Materials and Methods

Materials. Dodecyltrimethylammonium bromide ($C_{12}H_{25}N(CH_3)_3^+Br^-$) was purchased from Aldrich with purity greater than 99% and used as received. Silica gel for column chromatography was obtained from Aldrich and used without further purification. This silica gel has a BET surface area of 500 m^2/g and pore volume of 0.75 cm^3/g . The distilled H_2O used for the aqueous solutions was deionized and filtered by using a 0.45 μm nylon membrane.

FTIR Spectroscopic Measurements. Attenuated total reflection IR spectra were taken using a BOMEM Michelson MB-100 FTIR spectrometer with a liquid nitrogen cooled HgCdTe detector. ZnSe internal reflection elements were from Harrick Scientific Co. and had dimensions of 50x10x3mm and employed a 45° angle of incidence. The optical bench of the spectrometer was purged with dry nitrogen. Spectra of the samples were obtained with 256 scans at a resolution of 2 cm^{-1} . Figure 1 shows the flow cell developed and used in our laboratory to flow solutions past the silica particles. This flow cell is designed to fit into a standard ATR sample holder. Typically, the silica gel particles are introduced into the body of the flow cell and contained within the sample compartment (which comprises the space between the membrane and the ZnSe waveguide) by a membrane fabricated from a thin sheet of Al into which ca. 50 μm holes had been drilled. This membrane constrains the particles to press against the ZnSe waveguide. Then, the flow cell is pressed against a silicone gasket, and therefore, against the ZnSe waveguide using a screw press. In this configuration, the silica particles are pressed against the waveguide, and therefore, are within the evanescent wave region of the IR beam.

Before any spectra were taken, the cell with dry silica was placed into the sample chamber, which was then purged with dry nitrogen for 10 minutes. Then, a 2.7mM NaCl solution was pumped into the cell for 10 minutes at a flow rate of 2.5 mL/min., and the first single-beam spectrum was taken. This spectrum was used as the reference for all the sample spectra thereafter. Preliminary experiments had shown that an equilibrium could be reached at the silica gel surface after 10 minutes of exposure to a DTAB solution within the concentration range of 0.5 mM ~ 20 mM. Thus, each sample spectrum was taken after pumping a DTAB solution of a known concentration through the flow cell for 10 minutes at a flow rate of 2.5 mL/min. After the spectrum had been taken, a 2.7 mM NaCl solution was pumped into the cell for 10 minutes to wash out the adsorbed DTAB. Note that even the DTAB solutions contained 2.7 mM NaCl. The purpose of the use of low concentration salt solutions in these experiments was to provide for the charge compensation that is necessary whenever a charged species such as DTA^+ adsorbs or desorbs.

Results and Discussion

Figure 2a shows the spectrum of a 1 mM aqueous solution of DTAB at a bare ZnSe ATR element. This spectrum shows the CH stretching envelope that is characteristic of species with long alkyl chains. It also shows an envelope in the 1500 - 1700 cm^{-1} range. This

envelope is due to water absorption from the OH bending vibration, with small absorptions from water vapor in the spectrometer chamber superimposed on it. The appearance of this envelope is due to small changes in the amount of water within the region of solution probed by the beam. These changes arise both from changes in the mole fraction of water within the probed region between the background and the sample scans and from changes in the penetration depth between these two scans. This latter effect is caused by subtle changes in the refractive index of the solution due to changes in the solution composition. A full description of these effects will be reported in a forthcoming full paper. The important message to be garnered from the spectrum in Figure 2a is that the spectral region from 1500 to 1700 cm⁻¹ is relatively obscured by water features, which makes it difficult to use it for quantitative analysis of DTAB adsorption. Thus, the CH stretching features around 2800-3000 cm⁻¹ have been used instead, with spectral assignments made according to published data.¹⁵

Figure 2b shows spectra of DTAB of different concentrations in the presence of silica particles. The CH₂ symmetric stretch (ν_s) is observed at 2855 cm⁻¹. The CH₂ asymmetric stretch (ν_{as}) is observed at 2926 cm⁻¹. The bands are more clearly assigned in Figure 2c, which is for the 20 mM case. It is expected that the alkyl chain CH stretching vibrations should be essentially identical for the adsorbed and solution phase DTAB species^{13,16}, because the weak physisorption expected for this species is not likely to significantly perturb the alkyl chains. Thus, we have integrated the spectral region between 2846 and 2875 cm⁻¹ to quantitatively evaluate both species simultaneously.

Figure 3 shows the integrated areas of the spectral region between 2846 and 2875 cm⁻¹ for various concentrations of DTAB adsorbed on silica gel. Series 1 shows the experimental data. These integrated intensities include the contributions from both bulk solution and adsorbed DTAB. A method used by Simpson and Harris¹⁷ was applied to subtract the bulk solution contribution to the total intensity. Since the ATR intensity is proportional to concentration according to Beer's law,¹⁸ a linear regression was made to model the solution phase behavior. By fitting the high concentration points (2.5 mM~20 mM) to the linear model, the slope b and intercept a could be generated. The intercept was the intensity of the spectrum when DTAB reached saturated surface coverage, and the slope was the proportional factor in Beer's law. Thus the bulk solution contribution to the intensity could be generated by using

$$A_{\text{solution}} = b * C \quad (1)$$

where C is the concentration of the solution at equilibrium.

Figure 3, series 2 gives the integrated intensities after point-by-point subtraction of the solution contribution. These data clearly have the form of an adsorption isotherm, and suggest that the surface is saturated with DTAB at concentrations of 2.5 - 3.0 mM. In order to obtain a quantitative measure of the adsorption behavior, both the Langmuir and Frumkin models were used to fit this experimental adsorption isotherm. For both models, the

fractional coverage θ was obtained by normalizing the integrated intensities, i.e. each integrated intensity was ratioed to the extrapolated intercept a . For the Langmuir model

$$\theta = KC/(1+KC) \quad (2)$$

where K is the adsorption equilibrium constant, and C is the equilibrium concentration of the adsorbate, which, in an accurate definition, should be the activity of the adsorbate. However, given that the data in this case are significantly below the critical micelle concentration for DTAB, we have chosen to use the concentrations. The result of the Langmuir fit is shown in Figure 4a. The curve fit gives $K=1.6 \times 10^3 \text{ M}^{-1}$, using a non-linear least squares analysis.

Comparison of the experimental data points with the Langmuir fit in Figure 4 makes it clear that the Langmuir isotherm does not adequately describe the adsorption of DTAB at silica. Thus, one must consider the deficiencies of the Langmuir model, which is based on the following assumptions: (1) only a monolayer is formed at the surface; (2) the surface sites are homogeneous, in the sense that the adsorption energy is constant across the surface; and (3) no interactions occur between adsorbates.^{17,19,20,21} Consideration of the experimental points reveals that the first assumption is reasonable; the adsorption shows clear saturation behavior characteristic of monolayer formation. However, the validity of the remaining two assumptions is less obvious by simple inspection of the data. In order to test whether the inclusion of adsorbate interactions in the model would provide a better fit, a Frumkin model was then used. In the Frumkin model,

$$\theta/(1-\theta) = KC \exp(g\theta) \quad (3)$$

the isotherm is modified by an exponential factor, the physical meaning of which is that the adsorption energy is a function of surface coverage. If the interaction parameter, $g > 0$, the interaction between the adsorbates is attractive; if $g < 0$, it is repulsive.

The solid line in Figure 4 gives the result of a non-linear, least squares fit of the experimental data to a Frumkin model, with $K = 4.5 \times 10^3 \text{ M}^{-1}$ and $g = 2.4$, which suggests attractive interactions between adsorbed DTAB molecules, probably mediated by hydrophobic interactions between the alkyl chains. The regression coefficient, r , for the Frumkin fit is $r^2=0.93$, while the corresponding value for the Langmuir fit is $r^2=0.72$. Thus, the Frumkin fit is seen to be much better than the Langmuir fit.

Conclusion

An *in-situ* FTIR-ATR method has been described which can be used to quantitatively measure the adsorption of surfactants at the mineral/water interface. For DTAB, a monolayer is formed on the silica gel surface at concentrations near 2.5 - 3.0 mM. The adsorption can be modeled as a Frumkin isotherm. The shape of the isotherm suggests that the adsorption proceeds to saturation (i.e. monolayer formation) and then stops. The positions of the CH stretching peak maxima suggest that the adsorbed DTAB species form a relatively disordered structure on the silica surface. The positive interaction parameter, $g = 2.4$, can be interpreted as indicating that the adsorbed DTAB molecules attract one another.

This value of the Frumkin interaction parameter is in relatively good agreement with a value, $g = 2.1$, reported by Peng and Rusling²¹ for DTAB adsorption onto a Au electrode surface. Thus, even though the surfaces are distinctly different, this comparison reveals that the interactions between the alkyl chains are quite similar in these two cases.

A significant conclusion of this study is that the *in-situ* ATR-FTIR method provides a relatively facile route into studies of the adsorption of surfactants at the mineral-water interface. Thus, it is now possible to make comparable measurements on a wide variety of surfactant and mineral surface systems. In addition, it should be possible to use these methods to examine the interactions between these surfactant systems and the pollutants themselves²²⁻²⁵, an effort that is ongoing in our laboratories. Specifically, we are now examining the uptake on hydrophobic pollutants, such as TCE, into such surfactant layers in an effort to understand how to optimize this uptake.

Acknowledgment

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Figure 1 A side view of the special flowing cell developed and used in this experiment. Solution can flow through the silica particles at the ZnSe and silica interface, thus an in-situ spectrum can be obtained.

Figure 2 (a)Spectrum of 1mM DTAB when scan time is 1024 and resolution is 2 cm^{-1} . From this spectrum CH_2 stretches can be seen at $2800\text{-}2900\text{cm}^{-1}$. Those sharp peaks at $1400\text{-}1800\text{ cm}^{-1}$ are from water vapor in the IR chamber.

- (b) CH_2 stretches shown in various concentrations of DTAB.
- (C) Spectrum of 20mM DTAB at the region of $2850\text{-}3000\text{cm}^{-1}$. This spectrum shows both CH_2 stretches and CH_3 asymmetric stretch.

Figure 3 Spectroscopic isotherm of DTAB. Series 1 shows the integrated intensity at 2855cm^{-1} plotted vs. concentration of DTAB. Series 2 shows the isotherm after contribution of the solution part to the intensity has been subtracted.

Figure 4 Langmuir and Frumkin fittings of the isotherm. Both observation and statistic test show that Frumkin model fits better.

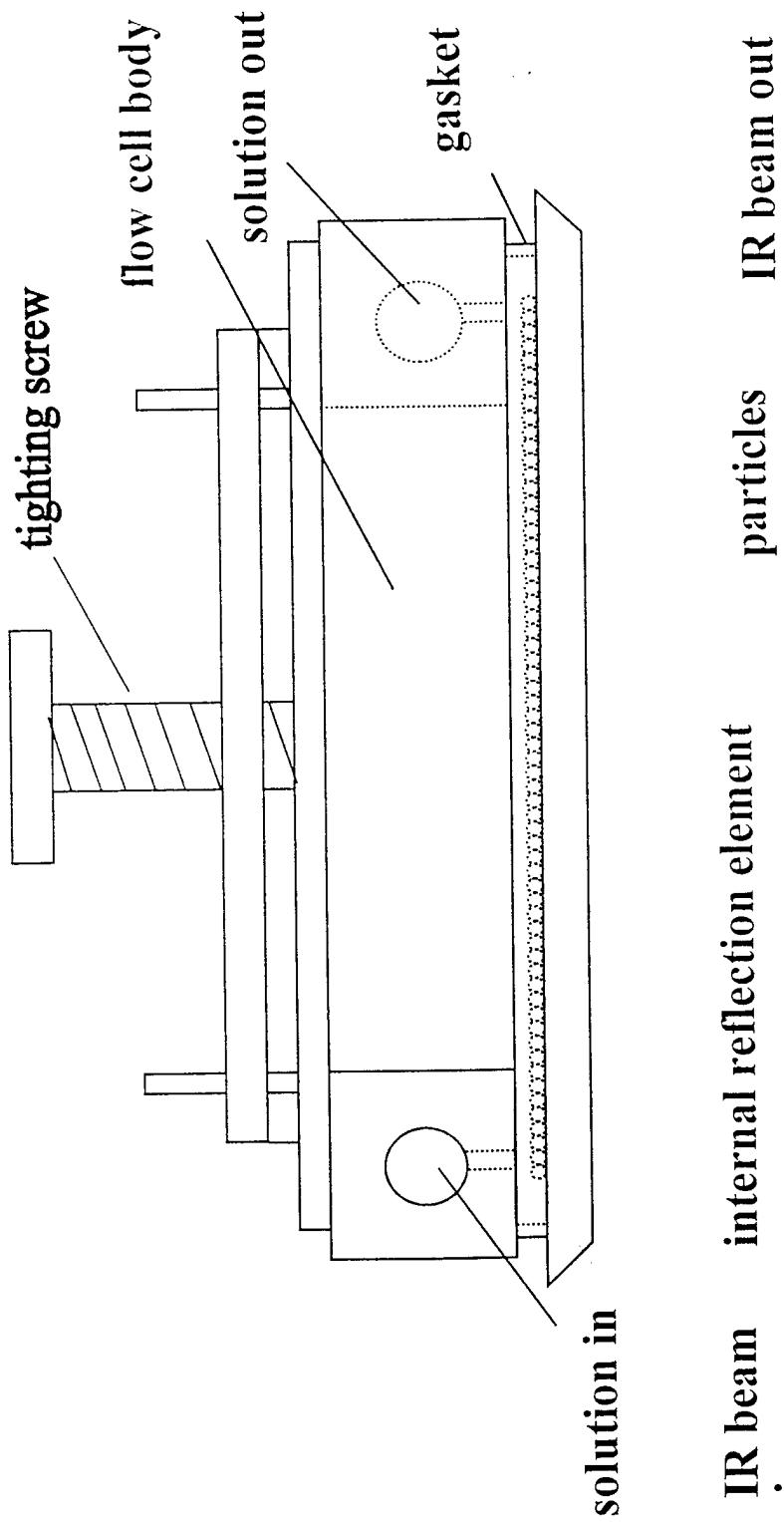


Figure 1

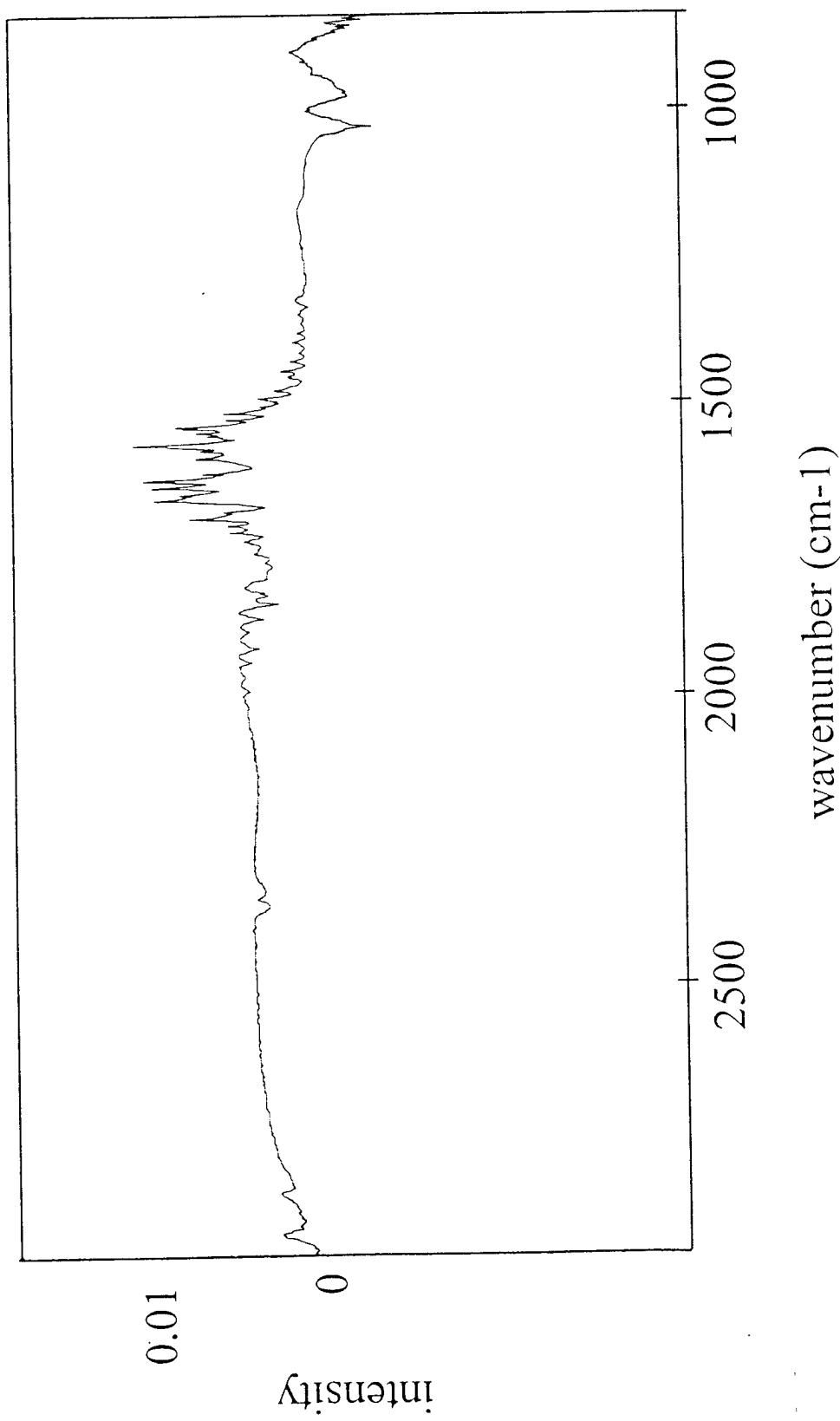


Figure 2a

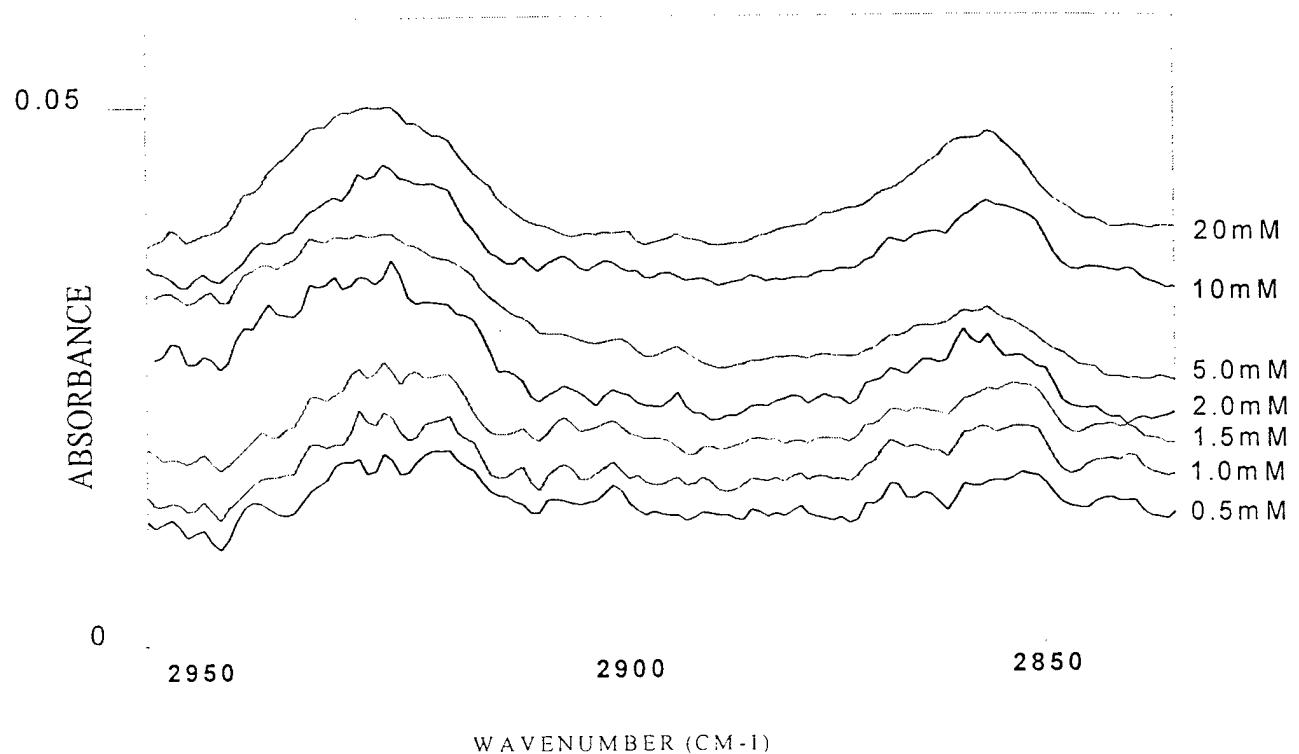
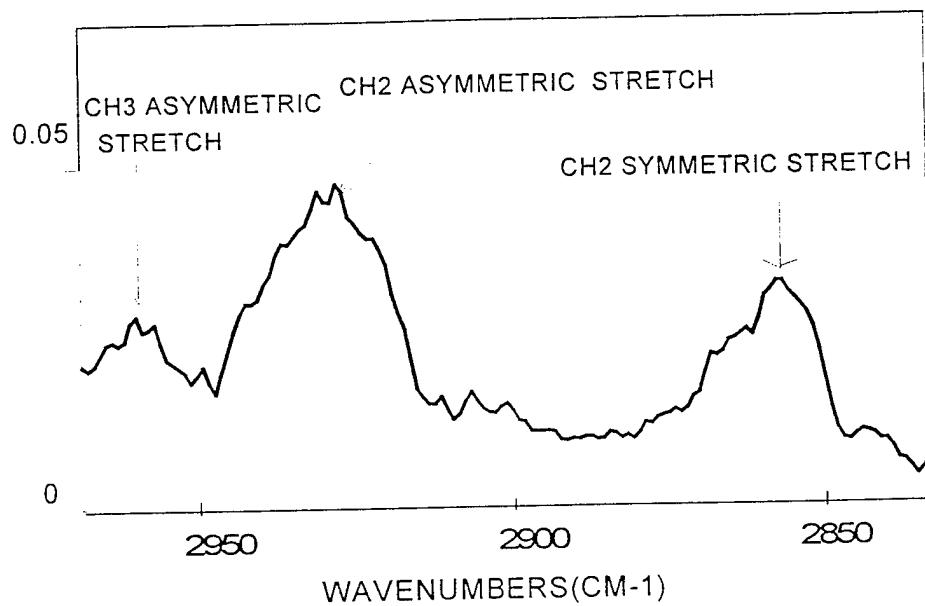


Figure 2b



ATR SPECTRA OF 20mM DTAB ADSORBED ON SILICA GEL

Figure 2c

ISOTHERM OF DTAB

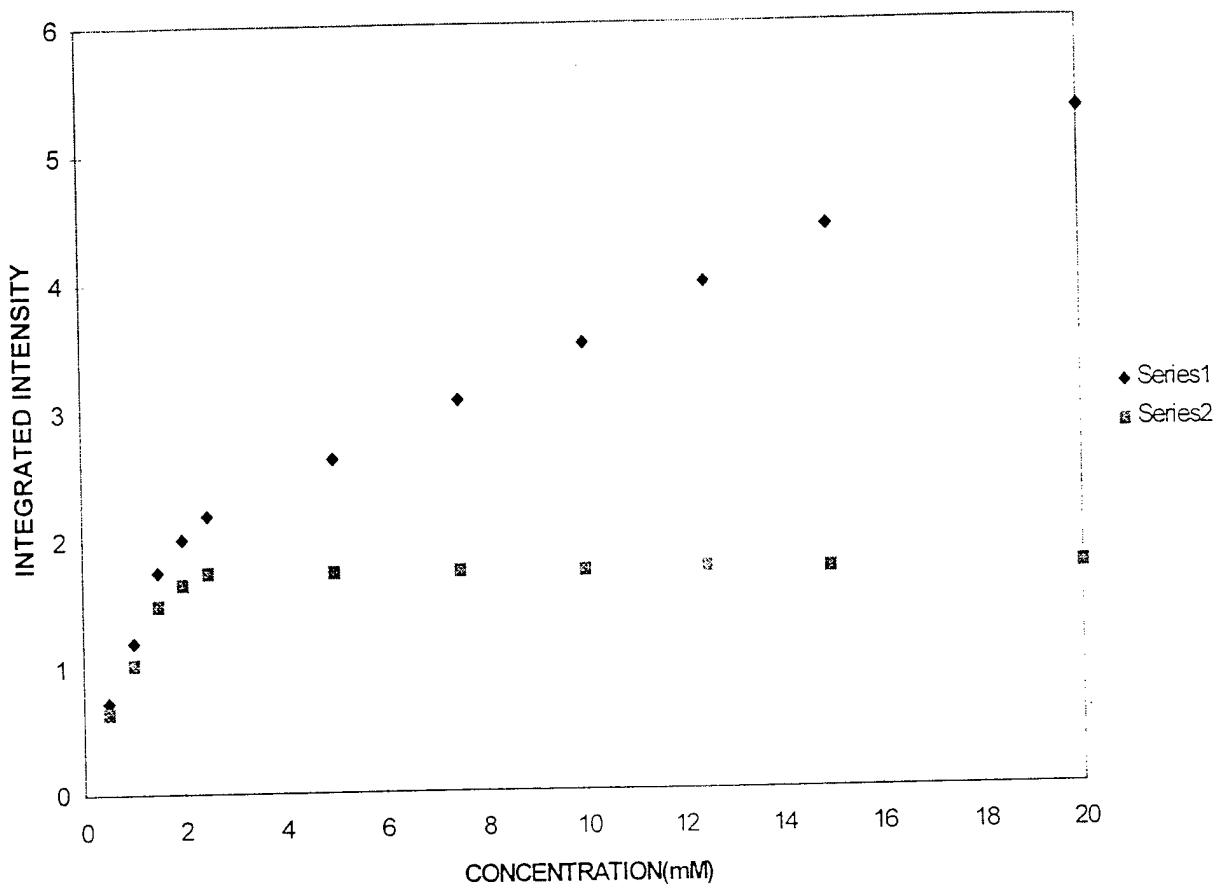


Figure 3

DTAB isotherm on SiO₂

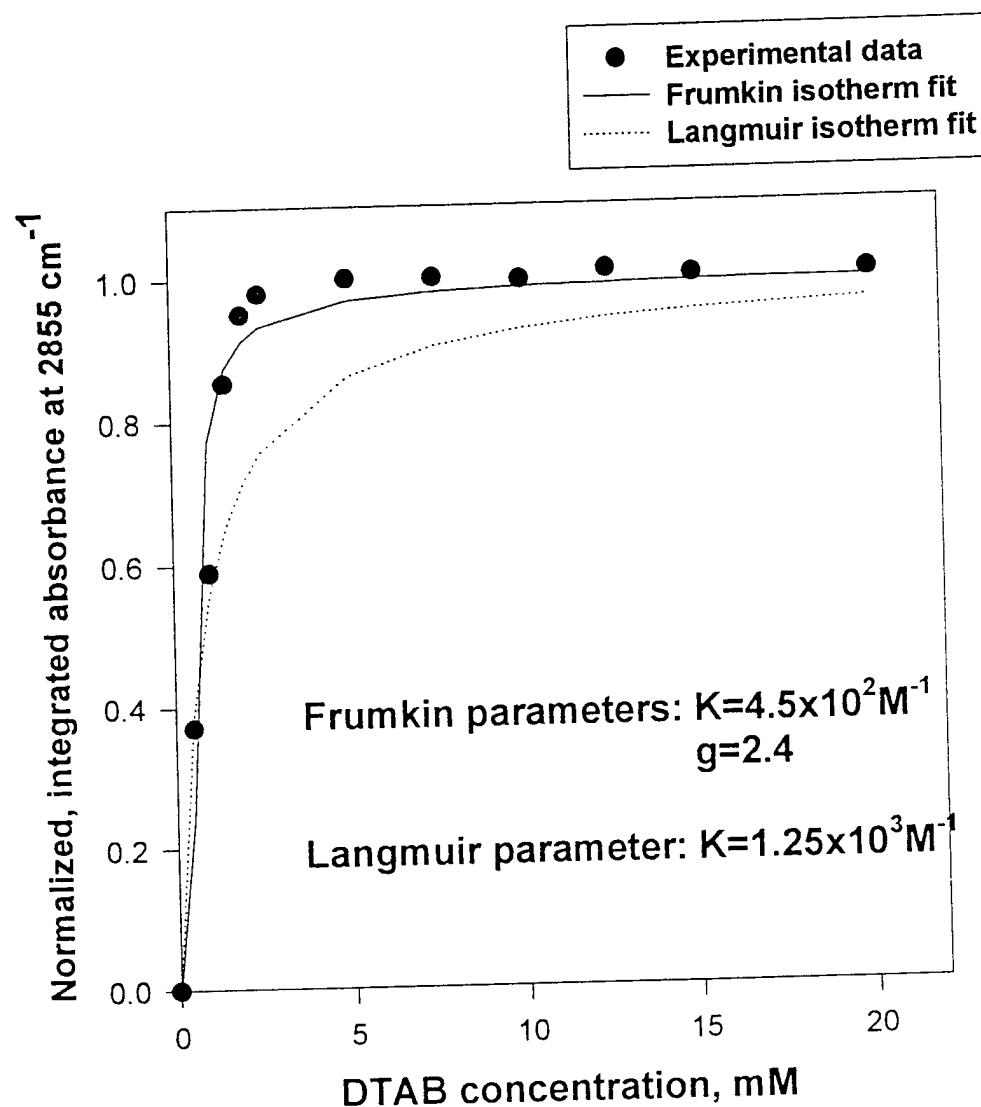


Figure 4

Mathematical Modeling: Summary Report
October 1997
Myron B. Allen, Department of Mathematics

Work on this aspect of the project began officially in January, 1995. The people involved include the following:

- Myron B. Allen, Professor of Mathematics
- Stacy Howard, Ph.D. candidate, Mathematics
- Patrick O'Leary, Ph.D. candidate, Mathematics.

The aim of the mathematical modeling part of the project was to characterize the effects of random, spatially varying adsorption on the transport of organic and inorganic groundwater contaminants.

More specifically, we view a soil column or a one-dimensional porous medium as an array of adsorption sites, with adsorption characteristics obeying a specified frequency distribution and having a specified spatial correlation structure. This model reflects the uncertainties associated with heterogeneous geologic media. Given this stochastic model of the porous medium, we investigate whether one can model the ensemble-average contaminant transport using a standard, advection-diffusion-type transport equation with "effective" (upscaled) coefficients to capture the effects of stochasticity.

The methodology used has been a combination of numerical and analytical investigation, based, for the time being, on the simple case of equilibrium adsorption according to a linear isotherm. We developed a finite-element code for the advection-diffusion-retardation equation with spatially varying retardation and a statistical algorithm for assigning retardation factors to cells in the grid from a probability distribution having specified mean, variance, and spatial covariance. This numerical scheme shows clearly that, when the adsorption characteristics are spatially correlated over distances comparable to the dimensions of the contaminant plume (or larger), the spreading of the average plume cannot be adequately modeled using the standard, Fickian model for hydrodynamic dispersion.

The analytical studies have pursued several tacks. One of the most fruitful has been small perturbation theory, in which we derive approximate equations governing the average plume by assuming that the retardation field has the form of a constant value plus a small, spatially varying fluctuation having mean zero. This approach yields a nonlocal, integrodifferential equation for the average contaminant plume. While this equation explains the non-Fickian behavior observed in the numerical studies, its nonlocal form is extremely inconvenient for numerical approximations, and therefore it is unlikely to find widespread use in applications.

The investigation has not ended, even though the funding period has. We are now investigating numerically tractable methods to solve for the average plume – methods that do not require the solution of nonlocal equations.

The work yielded the following publications and invited lectures:

PUBLISHED ARTICLES

P. O'Leary, M.B. Allen, and F. Furtado, "Groundwater transport with stochastic retardation," Proceedings, Third IMACS Conference on Iterative Methods, ed. by J. Wang et al., Jackson, WY, 9-12 July, 1997.

J. Yang, R. Zhang, J. Wu, and M.B. Allen, "Stochastic analysis of adsorbing solute transport in three-dimensional, heterogeneous, unsaturated soils," Water Resources Research 33:8 (1997), 1947-1956.

M.B. Allen and F. Furtado, "Computational methods for porous-media flows," Chapter 6, Advances in Fluid Mechanics: Porous-Media Flows, ed. by J.P. du Plessis, Computational Mechanics Publications, Southampton, U.K., 1997, 255-302.

J. Yang, R. Zhang, J. Wu, and M.B. Allen, "Stochastic analysis of adsorbing solute in two-dimensional unsaturated soils," Water Resources Research 32:9 (1996), 2747-2756.

B. Liu, M.B. Allen, H. Kojouharov, and B. Chen, "Finite-element solution of reaction-diffusion equations with advection," invited paper in Proceedings, Computational Methods in Water Resources XI, ed. by A. Aldama et al., Cancun, Mexico, 22-26 July, 1996, Computational Mechanics Publications, Southampton, U.K.

INVITED LECTURES:

"The three R's of groundwater contaminant transport," invited lecture at Third Workshop on Computational Methods for Oceanic, Atmospheric, and Groundwater Flows, Rio de Janeiro, Brazil, 15 September 1997.

"Numerical solution of reaction-diffusion equations with advection," invited minisymposium lecture, Second Panamerican Workshop on Computational and Applied Mathematics, Gramado, Brazil, 12 September 1997.

"Finite-element solution of reaction-diffusion equations with advection," invited minisymposium lecture, SIAM Geosciences Conference, Albuquerque, NM, 17 June 1997.

"The three R's of groundwater contaminant transport," invited lecture at the First Workshop on Large Scale Scientific Computation, Varna, Bulgaria, 7 June 1997.

"Finite-element solution of reaction-diffusion equations with advection," invited featured lecture at the Eleventh International Conference on Computational Methods in Water Resources, Cancun, Mexico, 26 July 1996.

"Scaling problems in underground solute transport," invited talk at Petrobras (Brazil's national oil company), Rio de Janeiro, Brazil, 21 July 1995.

"Combining streamline diffusion with characteristic timestepping in underground transport models" (with Biyue Liu), SIAM Geoscience Conference, San Antonio, TX, 10 February 1995.

"Scaling issues in the numerical simulation of advection-dominated flows in porous media" (with Frederico Furtado), SIAM Geoscience Conference, San Antonio, TX, 10 February 1995.

GRADUATE STUDENTS SUPPORTED:

Ms. Stacy Howard, Ph.D. candidate (left UW after giving birth).

Mr. Patrick O'Leary, Ph.D. candidate (dissertation in progress).

We accomplished the following tasks:

- We developed a one-dimensional finite-element model of solute transport, including the effects of equilibrium adsorption via a user-prescribed isotherm. The isotherm parameters can vary spatially.
- We developed a methodology for assigning random isotherm parameters (i.e. the adsorption field) according to a user-prescribed probability distribution.
- We made a large number of runs, based on different statistical realizations of the random adsorption fields, to test the hypothesis that random adsorption has a macroscopically dispersive effect, at least when the isotherm is linear. (Current work focuses on quantifying the apparent dispersion and extending the results to more realistic, nonlinear isotherms.)
- We began writing a modular code to solve the transport-adsorption equations in two space dimensions, where the performance of a numerical code is much more sensitive to the choice of numerical method used.